

HEMILABILE PHOSPHONATE-PHOSPHANE-Rh-CATALYSTS FOR HOMOGENEOUS AND HETEROGENEOUS CARBONYLATION

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Introduction

Mixed bidentate phosphane ligands such as ether-phosphanes [1-3], phosphane oxide-phosphanes [4], phosphanopyridines and amine-phosphanes [5] containing weak O- or N-donor groups and a strongly electron-donating phosphane group, are known to enhance activities or selectivities of Rh-catalyzed carbonylations. Also other transition metals form hemilabile O,P-chelated complexes, which have been extensively reviewed by Lindner [6]. A

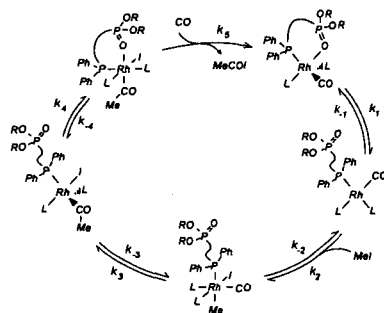
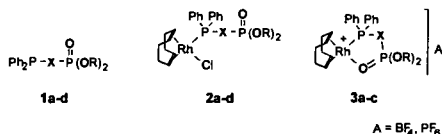


Fig. 1. Methanol carbonylation with hemilabile Rh complex catalysts

row of these complexes catalyzed not only carbonylations effectively but also hydrogenation [7], hydrosilylation [8], and ethylene polymerization [9]. The assumed function of the heterobidentate ligands in the rhodium catalyzed methanol carbonylation is illustrated in Fig. 1. It has been suggested that the oxygen-donating site of the bidentate ligand changes between a coordinated and an uncoordinated state during the catalytic cycle, thus forming chelate and open-chain metal complex structures [1,4]. The intramolecular generation and occupation of free coordination sites, stabilizing Rh-intermediates of different oxidation states and proceeding faster than according intermolecular processes, is assumed to accelerate rate-determining steps in the carbonylation route.

Rh-complexes with phosphonate-phosphanes [10] appeared as promising catalyst precursors because they form hemilabile complexes, which should enhance the necessary creation of free coordination sites in Rh^I-intermediates by ring-opening of chelate structures and ease the generation of the more oxophilic Rh^{III}-intermediates by O,P-chelate formation (Fig. 1). The concept of hemilabile catalysts with chelate structures involved in rate determining steps implies that the distance and structure between the phosphane and the phosphonate group should affect the carbonylation activity. Unlike the ether-, phosphane oxide-, amino- or pyridine- groups in previously described ligands [1-4], the phosphonate group should additionally facilitate a surface-anchoring of the transition metal complexes on oxidic materials such as silica or alumina, which is a necessary condition for stable slurry- and vapor-phase carbonylation catalysts. In this paper we wish to compare the new soluble Rh-complex catalysts 2a - d, derived from ligands 1a - d (Fig. 2), with known systems and report on the influence of the structure between strongly coordinated phosphane and weakly donating phosphonate moiety in homogeneous methanol carbonylation. Furthermore, we wish to report on supported hemilabile complexes and their properties in slurry- and vapor-phase methanol carbonylation.



	X	R
a	-CH ₂ -	ⁱ Pr
b	-CH ₂ CH ₂ -	Me, Et
c	-CH ₂ CH ₂ CH ₂ -	ⁱ Pr
d		ⁱ Pr

Fig. 2. Ligands and catalyst precursors

Experimental

The methylene bridged ligand 1a was accessible via reaction of LiCH₂P(O)(OⁱPr)₂ with bromodiphenylphosphane. Reaction of 2-chloro-ethyl-dimethylphosphonate or 3-bromo-propyl-diisopropylphosphonate with diphenylphosphane and potassium-tert.-butylate afforded the

phosphonate-phosphanes **1b** and **1c**. Reaction of the O,P-ligands with $[\text{ClRh}(\text{cod})]_2$ gave open-chain complexes, **2a - c** which could be easily converted with AgBF_4 or AgPF_6 into O,P-chelate structures **3a - c** (Fig. 2, Fig. 4). The structures of ligands and complexes were verified by MS, NMR and IR. A detailed report on preparation details and properties of the starting complexes will be given elsewhere [11].

Catalytic activities of the soluble Rh-catalysts were tested in a stirred 100 ml-autoclave made of stainless steel. During the catalytic runs, the autoclave-pressure was kept constant at 30 bar. To exclude air contact, the autoclave was filled using Schlenk-techniques with 100 mmol methanol, 6 - 48 mmol methyl iodide, 0.05 - 0.2 mmol rhodium complex and methyl acetate was used as solvent to reach a total volume of 25 ml. After pressurizing with CO (15 bar cold), the filled autoclave was heated up to reaction temperature between 120 and 195 °C and then the pressure was adjusted to 30 bar. The CO-consumption was calculated from the pressure decrease in a closed tank with a known volume which was connected to the autoclave via a pressure regulator. Carbonylation activity was calculated from the initial CO-conversion rate ($X_{\text{CO}} < 20\%$). A typical plot for the CO uptake vs. time is given in Fig. 3. The linearity of the plot clearly shows the zero-order of the substrate methanol and is in accord with the rate laws Eq. (1) and Eq. (2) below (p_{CO} , c_{Rh} , and $c_{\text{MeI}} = \text{constant}$). Second order rate constants k_i [$\text{l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$] were related to the concentrations of Rh and MeI.

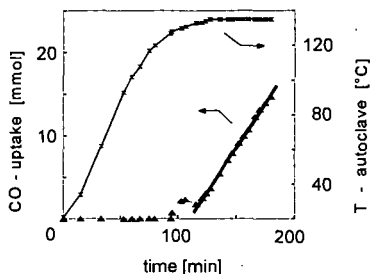


Fig. 3. Typical kinetic run

Results and discussion

The hemilabile character of phosphonate-phosphane-Rh complexes

The presumption for the catalytic concept has been preparatively confirmed for the phosphonate-phosphane-ligands. Both, cyclic and open-chain complexes were isolated after stoichiometric reactions (Fig. 4) at mild conditions. For instance, $(\text{cod})\text{RhCl}(\text{pepe})$ is smoothly converted with AgBF_4 into the halogene-free chelate complex at room-temperature and the ring-opening is easily achieved with CO at room-temperature under atmospheric pressure. Reversibility of the last process under reaction-like conditions is assumed from IR investigations of supported complexes. IR shifts in the stretching band of the phosphoryl group $\nu_{(\text{P}=\text{O})}$ to lower values in **3a - c** (KBr-wafer or solution), indicate the coordination of phosphoryl oxygen.

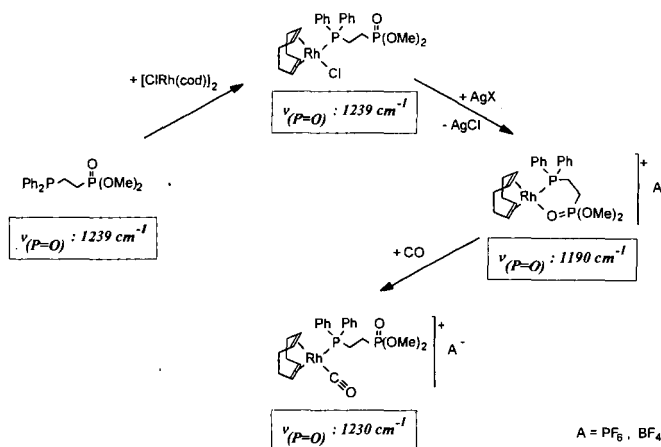


Fig. 4. Preparation and IR - data of catalyst precursors

^{31}P NMR data are depicted in Tab. 1. Not surprisingly, the shift in the ^{31}P NMR signal for the phosphane group ($\delta_{\text{phosphane}}$) shows that this group is coordinated in the open-chain complexes. The chelate structure of **3a - c** is confirmed by low field shifts of the phosphoryl-phosphorus signal ($\delta_{\text{P}=\text{O}}$, compared to **1a - c**, **2a - c**) and additionally by coupling with rhodium ($J_{\text{P-Rh}}$). Considering the IR spectra of **3a - c**, it is concluded that the $\text{P}=\text{O}$ - groups and not the $\text{P}-\text{O}-\text{R}'$ - groups act as oxygen donors.

Table 1. NMR data of ligands and Rh complexes

	$\delta_{P=O}$	J_{PORh}	J_{PP}	$\delta_{Phosphane}$	J_{PRh}
ligands					
1a	24.91 (d)	-	45.9	-25.32 (d)	-
1b	34.50 (d)	-	62.0	-12.10 (d)	-
1c	29.71 (d)	-	2.9	-17.37 (d)	-
open-chain complexes					
2a	21.33 (d)	-	16.9	21.51 (dd)	156.8
2b	32.80 (d)	-	63.0	26.80 (dd)	150.0
2c	29.28 (d)	-	4.9	26.60 (dd)	151.6
chelate complexes					
3a	48.85 (dd)	5.7	50.8	14.69 (dd)	149.6
3b	38.79 (dd)	2.9	13.1	21.21 (dd)	154.0
3c	40.13 (d)	8.1	-	23.74 (dd)	153.5

Catalytic properties of the hemilabile catalysts in homogeneous methanol carbonylation

The methanol carbonylation to acetic acid can roughly be formulated as a sequence of rate determining oxidative addition of the promoter Mel, methyl group migration to a CO-ligand and reductive elimination of acetyl iodide induced by CO-attack (Fig.1). The promoter is regenerated from methanol and HI, the last being liberated in the fast and irreversible proteolysis of acetyl iodide. Second order rate constants in a temperature range between 120 and 195 °C were obtained for various Rh-complexes in autoclave experiments monitoring the CO-consumption. The resulting activation parameters are summarized in Tab.2.

Table 2. Ligand effects on activation parameters of the Rh-catalyzed methanol carbonylation

	active carbon	cod	PPh ₃	dppe	1a	1b	1c	1d
ΔH^\ddagger [kJ/mol]	20.4	67.5	54.9	27.5	38.6	55.2	61.8	76.0
\pm	9.2	13.1	5.4	6.2	3.4	5.2	5.3	9.1
ΔS^\ddagger [J/mol/K]	-233	-112	-141	-211	-179	-141	-126	-90
\pm	22	32	13	15	8	12	12	22

cod - 1,5-cyclooctadiene, PPh₃ - triphenylphosphane, PPh₃:Rh = 2:1, dppe - bis(diphenylphosphano)ethane

The activation enthalpies in Tab.2 differ significantly over a wide range, but a general superiority of the hemilabile catalysts compared to known systems can not be postulated. With the data given here, one can choose certain temperatures to show the superiority of the hemilabile catalysts and the opposite can be done at another temperature, which may illustrate the sometimes questionable comparison of activities at one more or less arbitrary chosen temperature. It is interesting that activation enthalpies of hemilabile catalysts increased with growing distances between phosphonate- and phosphane-group. The highest activation enthalpy was obtained with the p-phenylene-bridged phosphonate-phosphane 1d, which can not form chelate complexes. This indicates that chelate structures are involved in one of the rate-limiting steps. The additionally to the oxidative Mel- addition emerging rate-limiting steps in P-ligand systems (see also Fig 5) can be the reductive elimination of acetyl iodide ($k_4 \cdot k_5$) or methyl-group migration (k_3). With the given kinetic data, none of these alternatives can clearly be appointed to be more likely.

The hemilabile complex precursors showed generally higher activation entropies than the Rh-bisphosphane complex precursor. This is explained with the generation of open-chain structures of the phosphonate-phosphane complexes during the oxidative addition step, creating additional degrees of freedom for bond-rotation and vibrations. The apparently low activation enthalpy estimated (from only three points) for Rh supported on active carbon is probably caused by diffusion control. Observations in the vapor-phase methanol carbonylation confirmed this assumption.

It has to be stated here, that Tab. 2 shows apparent parameters, which do not merely reflect the rate determining oxidative addition of Mel as known for phosphane-free systems (e.g. cod as ligand), where a simple rate law (Eq. (1)) can be applied.

$$r = - \frac{dn_{CO}}{dt} = f(c_{Mel}) = k \cdot c_{Mel} \cdot c_{Rh} \quad (1)$$

The general case, considering additional rate-determining steps to the oxidative Mel addition, is a more complex function (Eq. (2)). This rate law has been derived from Fig. 1 applying network techniques [12] and covers also Eq. (1) as a special case (when $B \gg A \cdot c_{\text{Mel}}$).

$$\frac{1}{r} = A + B \cdot \frac{1}{c_{\text{Mel}}} \quad \text{with} \quad (2)$$

$$A = \frac{k_5 p_{\text{CO}} (k_3 k_4 + k_1 k_4 + k_1 k_3 + k_1 k_3) + k_1 (k_{-3} k_{-4} + k_3 k_{-4} + k_3 k_4)}{k_1 k_3 k_4 c_{\text{Rh}} p_{\text{CO}}} \quad \text{and}$$

$$B = \frac{k_5 p_{\text{CO}} (k_3 k_4 k_{-1} + k_1 k_4 k_{-2} + k_1 k_3 k_4 + k_4 k_{-1} k_{-2} + k_{-1} k_{-2} k_{-3} + k_1 k_{-2} k_{-3}) + k_{-2} k_{-3} k_{-4} (k_1 + k_{-1})}{k_1 k_3 k_4 k_5 c_{\text{Rh}} p_{\text{CO}}}$$

Indeed, Eq. (2) describes the influence of Mel concentration on the activity for both phosphane-containing and phosphane-free catalysts satisfactory, while the simple power law (Eq. (1)) failed, when phosphanes (e.g. **1a**) served as ligands (Fig.5). The changed reaction order of Mel is probably caused by the enhancement of Mel-addition due to phosphane ligands, consequently making other steps relatively slower and partly rate-limiting.

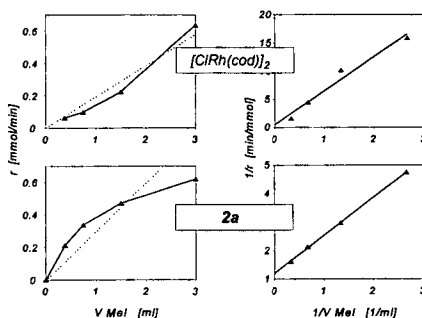


Fig. 5. Influence of Mel on the carbonylation rate; plots on the left side are derived from Eq. (1), on the right side from Eq. (2)

The new phosphonate - phosphane - complexes presented in this work were intended to be fixed on oxide surfaces via the phosphonate groups. While attempts of preparing stable complex-catalysts fixed on silica or alumina for slurry-phase reactions failed because of significant metal-leaching under carbonylation conditions, active carbon was found widely superior with respect to the leaching problem. In contrast to the results obtained for the homogeneous reaction, no significant ligand effects on the activation energies were observed, when the methanol carbonylation was conducted in the vapor-phase using active carbon supported complexes (Fig. 6). Normal diffusion of reactants begins to limit the activity of the supported Rh-complexes and leads to the observed uniform activation energies of about 30 kJ/mol.

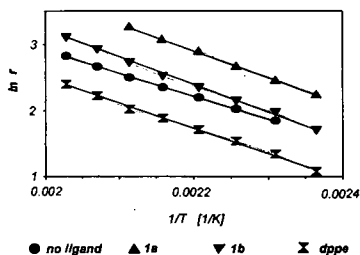


Fig. 6. Ligand effects on Arrhenius plots of active carbon-supported Rh-catalysts

IR-spectroscopic investigations of supported Rh-complex precursors revealed that the bisphosphane-ligand dppe hinders the formation of stable carbonyls (Fig. 7) and that the hemilabile ligands such as 2-(diphenyl-phosphano)ethyl dimethyl phosphonate (**2b**) form very stable monocarbonyl species, which are easily converted into dicarbonyl-species with increasing CO partial pressure even at elevated temperatures (Fig.8). The catalytic results in the vapor-phase suggest that phosphonate-phosphanes can also act as hemilabile ligands on supported catalysts.

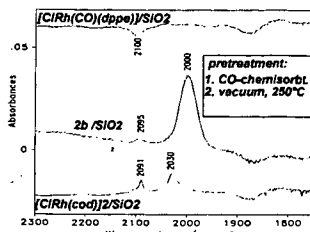


Fig. 7. FTIR spectra of supported Rh catalysts

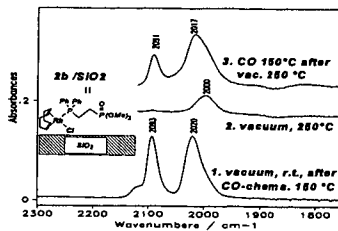


Fig. 8. Supported Rh-carbonyl species derived from 2b

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